On the non-Gaussian corrections in the self dynamics of semi-quantum fluids

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ABSTRACT

This paper is devoted to the study of the limits of the well-known Gaussian approximation in the self dynamics of quantum systems. After introducing the basic formalism and shortly reviewing the methods used in classical systems to apply corrections to the Gaussian approximation, an extension to quantum fluids is devised, with a particular interest in the so-called semi-quantum fluids, i.e. those in which the single particle momentum distribution approximately retains its Maxwellian form (but not its classical width). In this case a detailed correction scheme for both the short- and the long-time behaviors of the intermediate scattering function is proposed. Subsequently, a practical test of this approach is performed on a high resolution neutron scattering spectrum derived from liquid parahydrogen at $T = 14.1$ K. Extracting the spectral deviations from the Gaussian approximation with the help of an accurate centroid molecular dynamics simulation, we are able to describe them precisely and to derive the first two correction coefficients in this system by means of a simple fitting procedure. These experimental findings confirm the validity of our approach and show that a description of the self dynamics beyond the Gaussian approximation is necessary even in simple liquids affected by mild quantum effects.

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1. Introduction

Understanding the microscopic dynamics of liquid systems exhibiting moderate quantum effects (i.e. semi-quantum liquids), such as ^{4}He above the λ-transition, ^{3}He warmer than its Fermi temperature, molecular hydrogen, deuterium and tritium, neon, and their various mixtures, is still one of the open problems in condensed matter physics [1]. In general, semi-quantum liquids are fluid systems in which the actual temperature is lower than their Debye temperature [2]. However, differently from the highly-quantum fluids (e.g. superfluid ^{4}He and degenerate liquid ^{3}He), the corresponding quantum statistics (Bose–Einstein or Fermi–Dirac) seems to play no significant role in semi-quantum liquids [2], so that it is sensible to apply the Maxwell–Boltzmann statistics to describe their properties. Several theoretical approaches to the semi-quantum liquid dynamics have been tried in the past, but, despite some interesting results, none of them has come out as thoroughly satisfactory. On the computational side, *centroid molecular dynamics* [3] and *ring polymer molecular dynamics* [4] are surely among the simulation techniques producing the best results for semi-quantum liquids, but their scope is limited to evaluate the

time-correlation functions of operators linear in position, $\vec{r}(t)$, or momentum, $\vec{p}(t)$, only. The *Feynman–Kleinert linearized path-integral* does not seem to suffer these limitation [5], but its capability to precisely reproduce the dynamic structure factors of liquid hydrogen and deuterium is still matter of discussion [6]. Among the various promising approaches to the collective and the self dynamics of semi-quantum liquids, two kinds of methods are surely worth mentioning: those based on the so-called quantum generalized Langevin equation [7,8], which extend the mode coupling theory beyond classical systems, and those exploiting the analytic continuation of the imaginary time correlation functions, which make use of advanced maximum entropy methods [8,9]. Given this scenario, any precise experimental determination of dynamic quantities (i.e. time-correlation functions or their frequency spectra) that can be compared to the corresponding theoretical predictions becomes highly valuable, like, for instance, a recent experiment on liquid para-H_2 performed by the present authors [10].

The liquid parahydrogen system has been selected for two reasons: first because of its clear and evident semi-quantum character, which has attracted a number of theoretical studies, simulations and experimental works [10]. Secondly, because of the peculiar molecular hydrogen properties when H_2 is interacting with thermal neutrons: as explained in detail in the literature

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[11,12], it is possible to single out the self-dynamics of the para-H_2 molecular centers-of-mass in a condensed system by means of inelastic neutron scattering. In other words, the neutron scattering double-differential cross-section of a collection of para-H_2 molecules can be easily related to the self part of the center-of-mass dynamic structure factor, $S_s(Q,E)$ (with Q and E being the wave-vector and energy transfers, respectively), which is an intrinsic physical property of the system under investigation related to the single H_2-molecule dynamics. At this stage, it is a common practice to try to connect $S_s(Q,E)$ to the power spectrum of the velocity auto-correlation function. However, whenever $S_s(Q,E)$ is not available in a wide Q-range so that a low-Q extrapolation becomes impossible, this connection is attempted through the well-known Gaussian approximation (GA) [13]. The latter approach has been proved to be exact in some simple model systems: an ideal gas, a harmonic solid, and a fluid in which the particle diffusion is governed by classical hydrodynamics (i.e. the Fick's laws). Even though it has been found by some neutron scattering experiments [14] and simulations on classical fluid argon that there exist areas of the (Q,E) kinematic plane in which the Gaussian approximation does not hold precisely, this method is still widely used, and no complete critical assessment about its validity has been undertaken, especially in connection with semi-quantum liquids. In this respect, the mentioned work on pure liquid para-H_2 [10] was able to detect clear experimental evidences of a GA breakdown four times larger than in liquid Ar, possibly due to the more quantum nature of the former system. This scenario has prompted the authors of the present study to clarify some concepts about the applicability of the corrections to the Gaussian approximation in the case of a semi-quantum liquid, since the well-known approach set up for classical systems (Section 2) does not hold exactly for this class of systems. A simple correction scheme, complying with the main quantum properties, is presented (Section 3) after being carefully analyzed in its short time behavior. The rest of the paper will be devoted to a discussion of the model results in connection with a new analysis of published neutron scattering data [15] on liquid parahydrogen (Section 4), and, finally, to the conclusion and the perspective of the present work (Section 5).

2. The Gaussian approximation and its classical correction scheme

We have seen that one of the most important approaches to the self-dynamics problem is based on the so-called Gaussian approximation, which owes its name to the assumption that the self-intermediate scattering function [16], $I_s(Q,t)$, coincides with $I_{s,GA}(Q,t)$ given by:

$$I_{s,GA}(Q,t) = \exp\left(-Q^2 w(t)\right). \tag{1}$$

It is worth recalling that, in general, $I_s(Q,t)$ is just the time Fourier transform of the aforementioned $S_s(Q,E)$:

$$S_s(Q,E) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\exp\left(-iEt\hbar^{-1}\right)I_s(Q,t)dt, \tag{2}$$

where $\hbar$ is the Planck constant. Eq. (1) states that in the whole dynamical range between hydrodynamic diffusion ($Q \to 0$ and long times) and free-particle motion ($Q \to \infty$ and short times) there exists a function of time only, $w(t)$, that completely determines the motion of an individual particle. The GA finds its rationale in the fact that in a fluid Eq. (1) is valid in both the limit conditions above, so that large deviations from GA should not be reasonably expected at the nanometer–picosecond length and time scales relevant to molecular motions. In addition, we have already seen that the aforementioned formula is also exact for an isotropic harmonic

crystal and a highly diluted gas. Rahman et al. [13] have shown that in an isotropic system one can rigorously write:

$$I_s(Q,t) = \exp\left[\sum_{n=1}^{\infty}\left(-Q^2\right)^n \gamma_n(t)\right]. \tag{3}$$

Here:

$$\gamma_1(t) = -\frac{i\hbar t}{2M} + \frac{1}{3}\int_0^t (t-\tau)\langle\vec{v}(0)\cdot\vec{v}(\tau)\rangle d\tau, \tag{4}$$

where $\langle\vec{v}(0)\cdot\vec{v}(\tau)\rangle$ is the velocity auto-correlation function (VACF), and $\vec{v}(t)$ is the velocity of a tagged particle in the fluid. Eq. (4) also includes the free-recoil effect for particles of mass M. So the GA is obtained from the simple neglect of all $\gamma_n(t)$ with $n > 1$, the self-dynamics being then derivable from knowledge of $w(t) = \gamma_1(t)$ alone, through the use of its power spectrum, $f(\omega)$:

$$\gamma_1(t) = \frac{\hbar}{2M}\int_0^{\infty}\frac{f(\omega)}{\omega}\left[\coth\left(\frac{\hbar\omega}{2k_BT}\right)(1-\cos(\omega t)) - i\sin(\omega t)\right]d\omega, \tag{5}$$

which is defined [13] as:

$$f(\omega) = \frac{4M}{3\pi\hbar\omega}\int_0^{\infty}\text{Im}\langle\vec{v}(0)\cdot\vec{v}(\tau)\rangle\sin(\omega t)d\tau$$
$$= \frac{4M}{3\pi\hbar\omega}\tanh\left(\frac{\hbar\omega}{2k_BT}\right)\int_0^{\infty}\text{Re}\langle\vec{v}(0)\cdot\vec{v}(\tau)\rangle\cos(\omega t)d\tau. \tag{6}$$

However, in the classical case [16], Eqs. (4) and (6) can be simplified since $\gamma_1(t)$ and $\langle\vec{v}(0)\cdot\vec{v}(\tau)\rangle$ turn into real functions, symmetric in t:

$$\gamma_{1,cl}(t) = \frac{k_BT}{M}\int_0^{\infty}\frac{f_{cl}(\omega)}{\omega^2}(1-\cos(\omega t))d\omega = \frac{1}{3}\int_0^t (t-\tau)\langle\vec{v}(0)\cdot\vec{v}(\tau)\rangle_{cl}d\tau;$$
$$f_{cl}(\omega) = \frac{2M}{3\pi k_BT}\int_0^{\infty}\langle\vec{v}(0)\cdot\vec{v}(\tau)\rangle_{cl}\cos(\omega\tau)d\tau. \tag{7}$$

It is also straightforward to prove that $\gamma_{1,cl}(t)$ can be understood as one sixth of the mean square displacement of the tagged particle: $\gamma_{1,cl}(t) = \frac{1}{6}\langle(\vec{r}(t) - \vec{r}(0))^2\rangle_{cl}$. Due to the system isotropy, one can equivalently write: $\gamma_{1,cl}(t) = \frac{1}{2}\langle(z(t) - z(0))^2\rangle_{cl} = \frac{1}{2}\langle\Delta z(t)^2\rangle_{cl}$.

In the aforementioned classical framework, a detailed scheme for including corrections to the GA was set up by Nijboer and Rahman [17] by introducing appropriate time modulations of the power series for $\exp(-Q^2\gamma_{1,cl}(t)) - 1 + Q^2\gamma_{1,cl}(t)$. These are achieved, for example, through a set of $\alpha_{n,cl}(t)$ functions:

$$I_{s,cl}(Q,t) = e^{-Q^2\gamma_{1,cl}(t)}\left[1 + \alpha_{2,cl}(t)\frac{\left(Q^2\gamma_{1,cl}(t)\right)^2}{2!}\right.$$
$$\left. - \left(\alpha_{3,cl}(t) - 3\alpha_{2,cl}(t)\right)\frac{\left(Q^2\gamma_{1,cl}(t)\right)^3}{3!} + \cdots\right], \tag{8}$$

where $\alpha_{2,cl}(t)$ and $\alpha_{3,cl}(t)$ are related to the mean powers of the displacement of the tagged particle [18]:

$$\alpha_{2,cl}(t) = \frac{\langle\Delta z(t)^4\rangle_{cl}}{3\langle\Delta z(t)^2\rangle_{cl}^2} - 1;$$
$$\alpha_{3,cl}(t) = \frac{\langle\Delta z(t)^6\rangle_{cl}}{15\langle\Delta z(t)^2\rangle_{cl}^3} - 1. \tag{9}$$

This approach is largely used in various areas of condensed matter physics and physical chemistry including, for instance, polymers, complex liquids, and glasses [19,20]. However, being essentially a Gram–Charlier A series [21] for the self pair correlation function $G_s(r,t)$ (i.e. the spatial Fourier transform of $I_s(Q,t)$), it is not guaranteed to give probability density functions which are always positive and could exhibit convergence problems unless $G_s(r,t)$ decays to zero faster than a Gaussian distribution for r growing to infinity.